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(54) Regeneration of copper etch baths

(57) A copper etching process involves contacting copper with an aqueous etching solution comprising sulphuric acid and a peroxide, to which is added less than about 0.2% of an organic additive useful as a crystallization control agent and selected from ethylene glycol, propylene glycol and gum arabic.

REGENERATION OF COPPER ETCH BATHS

This invention relates to a method of using a copper etchant for the removal of copper from substrates such as printed circuit boards. In the production of such boards, conductive circuits are developed by forming a mask over a copper laminate, using an etch-resistant material such as a plastics material. The laminate is then exposed to a chemical which etches away the unprotected copper. A typical etchant is composed of hydrogen peroxide and sulphuric acid.

A substantial number of patent specifications describe various peroxide/sulphuric acid etchants, containing numerous additives intended to promote or accentuate certain properties of the etching solution. For example, various organic corrosion inhibitors such as saturated aliphatic acids or esters, sulphonates or sulphonic acids are disclosed in US-A-3,412,032. Catalysts such as urea or thiourea (US-A-3,668,131) or thiosulphate (US-A-4,462,861) are used to promote etching rates. A number of compounds are mentioned as stabilizers, including substituted aniline, sulphones and sulphanes (US-A-3,801,512) and oxy-quinoline (US-A-4,022,703).

US-A-4,141,850 recommends the use of a glycol as a promoter to enhance the dissolution rate of the etching solution in the presence of chloride or bromide ions. However, it discourages the use of either ethylene glycol or propylene glycol for this purpose. US-A-3,773,557 suggests the addition of ethylene glycol in an amount of 0.5% by weight per volume of the etching solution, but gives no explanation of its purpose in the solution.

US-A-4,437,931 describes the use of an acetylenic

diol as a promoter in a peroxide etching bath containing free Cl^- or Br^- ions. Examples of suitable promoters include 2-butyne-1,4-diol and 3-hexyne-2,5-diol.

5 The copper which is removed from the printed circuit board forms copper sulphate, which remains dissolved in the etch bath. As the concentration of copper sulphate in the etch bath increases, its presence tends to retard the etching rate of the bath.

10 To restore the efficiency of the bath, the copper sulphate is removed and the sulphuric acid and peroxide are replenished. A simple method of removing the copper sulphate is to chill the bath, thereby reducing the solubility of the copper sulphate and causing it to

15 crystallize and precipitate out as a solid. One way of chilling the bath is to transfer it from the treatment tank to an auxiliary tank, where refrigeration equipment is used to cool the solution from its operating temperature, in the range from 24° to 60°C

20 (75° to 140°F) to a temperature in the range from 0° to 10°C (32° to 50°F). At 50°C , the solubility of copper sulphate is 40 gms per 100 ml of water, whereas at 10°C , the solubility is about 17.4 gm/100 ml of water and, at 0°C , it is about 1/3 of its solubility at 60°C .

25 A problem arises, however, during the chilling of the solution, because, as it crystallizes the copper sulphate tends to deposit on the sides of the tank and crystal growth proceeds uninhibited until a hard layer of copper sulphate crystals is firmly deposited on the

30 equipment. Often, this layer must be removed from the equipment with chisels, pneumatic hammers or the like. Furthermore, the loose crystals which form on the bottom of the tank become too large to be removed by filtering. The unrestrained crystal growth is often

35 enhanced by the presence of the stabilizers in the etch

bath.

According to one aspect of this invention, a method is provided, for removing copper sulphate from a copper etch bath, normally operated at a temperature in the range from 23° to 60°C (75° to 140°F) and composed of hydrogen peroxide and sulphuric acid which comprises cooling the bath to crystalize out the copper sulphate, characterised in that the etch bath includes an amount in the range from 0.02% to 0.2% of a crystallization control agent selected from gum arabic and low molecular weight glycols having the formula $\text{HOCH}_2(\text{CH}_2)_X\text{CH}_2\text{OH}$ wherein X is 0 or 1.

This invention thus relates to a method of etching copper, e.g. in the preplate and pattern plate steps in the production of printed circuit boards. More particularly, it relates to the use of a small amount of an organic additive selected from low molecular weight glycols having the formula $\text{HOCH}_2(\text{CH}_2)_X\text{CH}_2\text{OH}$, wherein X is either 0 or 1, and gum arabic (acacia gum). The additive serves as a crystallization control agent. The two glycols represented by this formula are ethylene glycol and propylene glycol.

The organic additive is desirably present in the operating bath in an amount sufficient to control the size of the copper sulphate crystals which are formed in the bath, preferably in the range from about 0.02%. The bath can handle substantially greater amounts of ethylene glycol as indicated in US-A-3,773,557. When used within the preferred range, the glycol serves to keep the crystals of CuSO_4 in discrete particulate form, preventing the growth of the particles and their adhesion to the equipment. The crystals can be readily removed from the etch bath by filtration. Furthermore, the crystals which are formed are sufficiently pure to be used as a source of copper for electroless or

electrolytic plating.

The production of multilayer printed circuit boards involves many discrete steps, nearly all of which are important in producing an end product which performs in a totally satisfactory, fail-safe manner. A typical board construction comprises a laminate of copper foil sandwiched between layers of epoxy resin. The board is drilled to form holes which are metallized with copper to provide electrical contact between the two surfaces of the board. Both prior to and following the electroless and/or electrolytic plating of copper, the need arises to etch a certain amount of copper from the laminate. The board is subjected to a so-called pre-plate etch, to provide a clean surface which can be suitably activated for the deposit of electroless copper. Following plating, a photo-resist or screen resist is applied, exposed and developed to form a circuit pattern. Again the board is etched to remove the copper from the exposed portions thereof, as one step in developing the circuitry through the laminate.

An etch solution is typically prepared by mixing together the following components:

| | | |
|----|--|-------------|
| | H ₂ SO ₄ - 66°Bé | - 10% |
| | Water | - 86% - 88% |
| 25 | Micro-etch concentrate | - 2% - 4% |

This concentrate is prepared by blending together the following components:

| | | |
|----|-------------------------------------|-------------|
| | H ₂ O ₂ (50%) | - 90% - 95% |
| | Peroxide stabilizers | - 1% - 5% |
| 30 | Crystallization control agent | - 1% - 5% |

The crystallization control agent is preferably heated to an elevated temperature, at which the stabilizers can be dissolved, and the stabilizers are added with mixing. The mixture is then cooled down to

room temperature and the peroxide is blended in to give the concentrate.

The peroxide stabilizer or mixture of stabilizers is selected from the group of compounds which traditionally are used for the specific purpose of chemically or physically retarding decomposition of the peroxide. A number of these were described in the aforementioned patents and include the following:

- 10 Lower saturated aliphatic alcohols, such as methanol, ethanol, propanol and butanol;
- phosphoric acid;
- protein;
- 15 arylsulphonic acids, e.g. phenol-sulphonic acid, sulphosalicylic acid, toluene-sulphonic acid;

Etch rate improvers, promoters or catalysts may be added to the bath and typically include:

- 20 metallic ions of silver, mercury, palladium, gold and platinum;
- phenacetin, sulphathiazole or silver ions alone or with dibasic acids, phenyl ureas, benzoic acids, urea or thiourea;
- camphor; acetophenone; quinones;
- 25 acetylenic diols; and organic acids such as propionic acid, acetic acid, butyric acid.

The concentrations of the peroxide, stabilizers and control agent in the bath, based on a usage in the amount of 2% to 4%, cover the following range:

| | |
|--------------------------------|-----------------|
| H ₂ O ₂ | - .9% to 1.9% |
| Stabilizers | - 0.02% to 0.2% |
| Crystallization control agent- | 0.02% to 0.2% |

For use in the pre-plate etching of the board, the micro-etch concentrate is used in an amount of 3-4% to

produce a bath which, when operated at a temperature of 110°-120°F (43°-40°C) is capable of achieving an etch rate of about 70 micro-inches per minute. When used as a pattern-plate etch, the concentrate is used at a level of 2-3% at a lower temperature of 75°-85°F (24°-29°C) to give an etch rate of 6 micro-inches.

In either application, the solution can be loaded up to about 1 square foot (900cm²) of treatable surface area per gallon of etchant. The solution preferably is agitated mechanically or the board is moved or slowly oscillated in the bath to improve the through-hole etching capability of the solution.

As the etch solution is used, the concentration of copper sulphate dissolved in the solution builds up, gradually approaching saturation. This is best determined by analyzing for copper sulphate and comparing the concentration with the saturation point for copper sulphate at the bath operating temperature. Less accurate means may also be used, such as colorimetric procedures to measure the increase in colour intensity of the etch bath in proportion to the build-up of dissolved copper sulphate. Yet another method is to plot the decrease in the micro-etch rate as a function of copper sulphate build-up. As the concentration approaches saturation, etching is interrupted and the etch bath is treated to crystallize and remove a substantial amount of copper sulphate. The treatment consists of removing the solution from the etch tank, preferably by pumping it into an auxiliary tank equipped with a cooling coil to lower the temperature of the solution to a temperature in the range from 2° to 10°C (35° to 50°F) and preferably of 4° to 7°C (40° to 45°F). Alternatively, the crystallization can be carried out in the etch tank by shutting down the etching operation, cooling the

solution and removing crystals after formation. Because the etching of copper with peroxide is an exothermic reaction, the etch tank normally is equipped with auxiliary cooling coils to maintain the bath at a constant temperature. Thus, means for cooling the bath are already present.

In any event, after the crystals of CuSO_4 have been removed from the bath, it is adjusted as needed to replenish the H_2SO_4 and peroxide levels before re-use.

10 The copper sulphate crystals are sufficiently pure to permit them to be used as a source of copper for the preparation of electroless and/or electrolytic copper plating solutions. Typically, from 50%-75% of the copper sulphate is crystallized out and removed from

15 solution during each treatment, depending on the temperature to which the bath is chilled and the degree of saturation at the start of the treatment.

To more fully illustrate the invention, but without being limited thereby, the following example is given.

20

Example

A micro-etch bath is prepared, having the following composition on a weight basis:

| | | | |
|----|-------------------------|---|-----------|
| | Water | - | 86% - 87% |
| | Sulphuric acids - 66°Bé | - | 10% |
| 25 | Micro-etch concentrate | - | 3% - 4% |

The concentrate is composed of the following:

| | | | |
|----|---|---|-----|
| | H_2O_2 (50% solution) | - | 90% |
| | Stabilizers - proprietary | | 5% |
| | blend of sodium salicylate, | | |
| 30 | phenol sulphonate, a fluorocarbon and a | | |
| | wetting agent | | |
| | Ethylene glycol | - | 5% |

and is prepared by heating the ethylene glycol to 150°F (65°C), adding the proprietary blend of stabilizers

35 with agitation and cooling down to room temperature

Before adding the hydrogen peroxide. The concentrate is then mixed with the dilute sulphuric acid immediately prior to use. The bath is heated to a temperature of 40°C (120°F) and a printed circuit board is placed in the bath. The bath is mechanically agitated or alternatively the board is moved in the bath to increase the amount of etchant going through the holes drilled in the board. The boards are retained in the bath for a time of 1/2 to 3 minutes to
10 remove from 35-210 micro-inches of copper. Etching is continued until the bath contains 70-80 gms of copper per litre of bath, after which the bath is pumped into an auxiliary tank where it is cooled to 40 to 70°C (40°-45°F) to crystallize out the copper sulphate. The
15 presence of the minute amount of ethylene glycol appears to limit the amount of crystal growth which occurs, while at the same time preventing the crystals from adhering to the sides of the auxiliary tank.

It can be seen from the Example that the actual
20 concentration of ethylene glycol in the etch bath is very low, approximating to 0.15% to 0.20% by weight. As previously indicated, the amount of glycol or gum arabic in the micro-etch concentrate can be as low as 1%. Inasmuch as the amount of the concentrate present
25 in the etch bath can range from 2% to 4%, the effective concentration of the crystallization control agent in the bath can be as low as 0.02% by weight.

Although the Example describes the inclusion of the crystallization control agent in the initial bath make-
30 up, the invention can also be practised by adding the gum arabic or low-molecular weight glycol to the bath at an intermediate state or immediately prior to crystallization, ensuring, of course, that the agent is uniformly dispersed throughout the bath before
35 cooling.

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CLAIMS:

1. A method of removing copper sulphate from a copper etch bath, normally operated at a temperature in the range from 23° to 60°C (75° to 140°F) and composed of hydrogen peroxide and sulphuric acid, which comprises cooling the bath to crystallize out the copper sulphate, characterised in that the etch bath includes an amount in the range from 0.02% to 0.2% of a crystallization control agent selected from gum arabic and low molecular weight glycols having the formula $\text{HOCH}_2(\text{CH}_2)_x\text{CH}_2\text{OH}$ wherein X is 0 or 1.

2. A method according to claim 1, wherein the bath is transferred from an etch tank to an auxiliary tank, after which it is cooled to a temperature in the range from 2° to 10°C (35° to 50°F).

3. A method according to claim 2, wherein the bath is cooled to a temperature in the range from 4° to 7°C (40° to 45°F).

4. A method according to any preceding claim, wherein the control agent is added to the bath during the make-up of the bath.

5. A method according to any preceding claim, wherein the control agent is ethylene glycol.

6. A process of regenerating an aqueous copper etch bath composed of:

H_2SO_4

H_2O_2 .

stabilizers for the H_2O_2 , and

a crystallization control agent,

the bath being prepared by blending the stabilizers together with the control agent at an elevated temperature, cooling the blend and mixing the blend with H_2O_2 to give a concentrate, mixing the concentrate with H_2SO_4 to give a bath useful at a temperature in

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the range from 23° to 60°C (75° to 140°F), characterised in that the bath is cooled to crystallize out copper sulphate formed during etching and the growth of copper sulphate during crystallization is limited.

7. A process according to claim 6, wherein the crystallization control agent is selected from gum arabic and low molecular weight glycol having the formula $\text{HOCH}_2(\text{CH}_2)_X\text{CH}_2\text{OH}$ wherein X is 0 or 1.

10 8. A process according to claim 6 or 7, wherein the control agent is present in the bath in an amount in the range from 0.02% to 0.2%.

9. A process according to any of claims 6 to 8, wherein the bath is cooled to a temperature in the
15 range from 2° to 10°C (35° to 50°F)